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Reduction of Odorous Emissions from Kraft Pulp Mills  
Using Green Liquor Dregs

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**Reduction of Odorous Emissions from Kraft Pulp Mills  
Using Green Liquor Dregs**

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**Abstract**

This study is investigating the use of mill-generated green liquor dregs to reduce H<sub>2</sub>S emissions in mill waste gas streams to concentrations below the odor threshold. To be able to implement a process technology that employs a sorbent (i.e., dregs) that is self-generated, readily available, and does not produce a secondary waste stream that requires additional treatment should be an attractive low-cost alternative.

Bench-scale experiments using mill-derived dregs in a packed-bed reactor have determined the extent of H<sub>2</sub>S removal as a function of temperature, gas flow rate, H<sub>2</sub>S concentration in the feed gas, and residence time. Preliminary process calculations for a typical 1000 T/D recovery boiler show that the daily production rate of dregs can reduce H<sub>2</sub>S emissions to the required parts per billion level if the dregs can be regenerated and reused in a second cycle of H<sub>2</sub>S removal. Accordingly, a method using weak wash has been developed to meet this requirement, effectively further closing the mill sulfur balance. The spent dregs would still be landfilled.

Plans are under-way to reconfirm the laboratory results under actual mill operating conditions at several TRS emissions source points and establish the technical and economic attractiveness of the technology.

## INTRODUCTION

Odor is becoming an increasing concern of communities located near kraft pulp mills. The time is coming when the characteristic reduced sulfur odor will no longer “smell like money.” Previous odor-reduction technologies that have been investigated have centered around incineration and wet scrubbing, neither of which is looked upon in today’s environmentally conscious society as an acceptable route, with both technologies posing their own clean-up needs. No commercially feasible technology exists at present that eliminates the odor without creating a byproduct waste stream requiring additional treatment.

Installing any process to reduce or eliminate odor from a kraft mill will increase capital and operating costs without an accompanying productivity or efficiency increase. A process step that employs a sorbent that is essentially free, readily available, and does not produce a secondary waste stream that requires additional treatment should be an attractive low-cost alternative. Potentially, green liquor dregs is provide such a material.

The goal of this study was to determine the feasibility of using dregs to reduce total reduced sulfur (TRS) emissions from various sources in the pulp mill by a factor of 1000. This was governed by point sources, such as the recovery boiler, lime kiln, dissolving tank, and pulp washer, that emit TRS at ppm levels, together with the need to go to ppb levels to get below the human threshold limit.

The bench-scale effort reported here used a packed-bed reactor to determine the extent of  $\text{H}_2\text{S}$  removal as a function of several process parameters, including temperature, feed-gas  $\text{H}_2\text{S}$  concentration, gas flow rate, and residence time. The effective lifetime of the bed was determined, and a method to regenerate the dregs material for reuse was investigated. If, by chance, the dregs produced daily could remove all of the TRS emitted, then economics might suggest not regenerating the dregs, but simply continuing to use fresh material and sending the spent dregs to the landfill.

Longer term, this study hopes to determine the mechanism of reduced sulfur species removal, be it neutralization, catalytic oxidation, or physical adsorption. Dregs typically contain low concentrations of several metals (Ca, Mn, Mg, Fe, Al, Si, Na), some of which may be catalytically active, along with some unoxidized carbonaceous material, which can be expected to be in a highly activated state for gas adsorption. The pH of dregs is greater than 11.0, and hence, dregs could neutralize an acid gas such as  $\text{H}_2\text{S}$ . It is important from the point of view of reactor design to determine which mechanisms are involved.

The literature in the 1970’s actively promoted using conventional adsorbents and supported catalysts to eliminate sulfides and mercaptans in waste gases (1-7). Alley (1) looked at  $\text{H}_2\text{S}$  adsorption and oxidation on activated carbon, while Murray (7) used an iron oxide catalyst. Ross and Sood (4) reported on oxidation of  $\text{CH}_3\text{SH}$  over cobalt molybdate. More recently, Watt (8) reported on low-temperature catalytic oxidation of VOC’s (including dimethyl sulfide) over cobalt molybdenum oxide.

Bhatia et al. (5) researched wet scrubbing of recovery boiler stack gases as an alternative to black liquor oxidation for TRS control. They used alkaline suspensions of activated carbon in both an adsorption and an oxidation mode. Interestingly, they also tried 1% dregs in a 2% aqueous sodium carbonate suspension to scrub TRS gases. This was followed up by Andreyev and Jakovlev (9) who reported on the kinetics of  $\text{H}_2\text{S}$  oxidation in an alkaline suspension of "green liquor sludge from the paper industry."

These studies led to some scouting experiments at IPST to see if green liquor dregs in dry form could be used to treat gaseous  $\text{H}_2\text{S}$  in a packed-bed configuration (10). The results were qualitatively very positive and served as the basis of the Georgia TIP<sup>3</sup> program funding for the present work. A premixed air- $\text{H}_2\text{S}$  gas flow was passed through a 38-cm-long section of 2.5-cm tubing packed with 51 g. of dried dregs at 175°C. Feed gas mixtures of 40 ppm  $\text{H}_2\text{S}$  were rendered qualitatively "nondetect" in the product gas stream using lead acetate paper.

A recent study (11) reported the use of calcium hydroxide to react with  $\text{H}_2\text{S}$  to remove it from a gas mixture. Regeneration of the calcium salt was done by reacting the  $\text{CaS}$  formed with caustic, forming  $\text{Na}_2\text{S}$  that then could be combined with white liquor.

## EXPERIMENTAL

The initial focus of this study was to look at removal of  $\text{H}_2\text{S}$  from a  $\text{N}_2/\text{O}_2$  mixture using a packed-bed reactor containing dregs particles. Near the end of the work, dimethyl sulfide (DMS) was briefly investigated as an organic TRS component. Using this configuration, a family of "breakthrough" curves was generated to determine the effectiveness of the particles in removing the TRS component. A breakthrough curve shows the time it takes to "deactivate" the bed, as seen by the eventual appearance of detectable levels of the TRS component emerging in the product gas stream. By following the gradual increase in TRS concentration with time after breakthrough, kinetic rate data can be obtained that are useful for subsequent design considerations.

Green liquor dregs were obtained from Champion International (Quinnesec, MI), MacMillan-Bloedel (Pine Hill, AL), and Weyerhaeuser Corporation (Oglethorpe, GA). The samples from Champion and Weyerhaeuser were from the dregs filter and hence contained some undetermined amount of lime mud precoat material, whereas the dregs from MacMillan-Bloedel were from the clarifier underflow and contained no lime mud. To remove any potential effects of residual green liquor on the dregs, all samples were washed with deionized water, filtered, and dried in a laboratory oven at 105°C. The resulting solids were then screened through a 10-mesh (1.91 mm dia.) and a 60-mesh (0.23 mm dia.) screen. The accepts from between the 10- and 60-mesh screens were used for further study.

Below is a schematic of the experimental setup.

**Figure 1. – Experimental Setup**

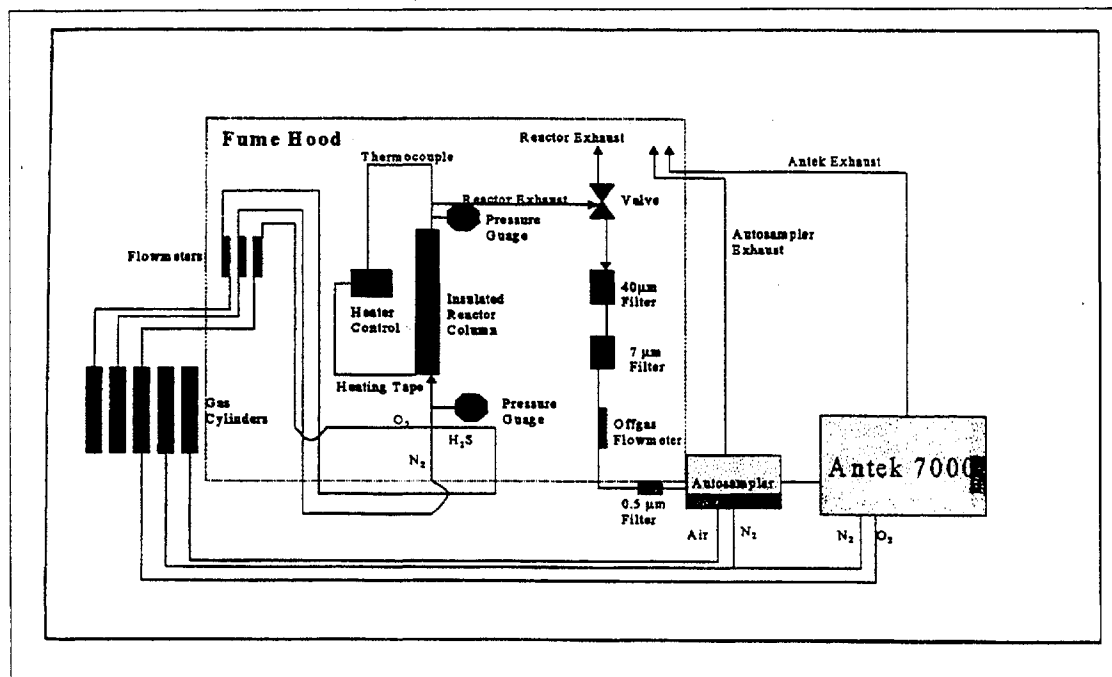


Figure 1 shows the flow of gases through 0.6-cm-diameter thick-walled 316 stainless steel tubing. The gases utilized were UPC nitrogen and zero-pure oxygen, 100 ppm hydrogen sulfide with balance as nitrogen, and air for autosampler valve actuation.

The reactor was made of 1.75-cm I.D. 316 stainless steel tubing about 46 cm long and was wrapped with adhesive-backed electrical heating tape and hot-water-pipe insulation with paper exterior to allow for rapid heating to the desired reactor temperatures. A 46-cm-long, 0.05-cm-diameter J-type thermocouple placed in a thermowell was inserted at the end of the dregs bed to monitor the bed temperature for the Chromalox 1603 temperature controller.

After first passing through two Nupro<sup>®</sup> gas filters of 40µm and 7µm, respectively, to remove any particulate matter that might have been present in the gas flow, the gas flow from the reactor was then passed through a Cole-Parmer model H<sub>2</sub>S flow meter to regulate the gas to the autosampler at 100 cc/min. After the offgas flow meter, the gas was passed through another filter of 0.5µm to remove any fine particulates before introduction into the autosampler.

Sample analysis entailed the autosampler capturing a 5-mL sample every 5 minutes and sending it to the Antek (Model 7000B) for total sulfur analysis by UV. The Antek instrument was calibrated for concentrations ranging from 0 to 100 ppm and has a

lower detection limit of  $\pm 1$  ppb. The calibration curve was estimated to be accurate to  $\pm 400$  ppb due to the use of multiple gas flow meters to make up the calibration gas mixtures. The form of the sulfur in the product gas was eventually checked with an independent GC-mass spec system.

The experimental parameters for this study were governed by the compliance levels for the mill sources of TRS emissions, including the recovery boiler and lime kiln stacks and the dissolving tank, evaporator condensate, and brownstock washer vents (11, 12). For instance, TRS compliance standards are 5 ppm for the recovery boiler and 80 ppm for the dissolving tank. Vent gas temperatures range from 100°C for a brownstock washer to just under 200°C for a recovery boiler. For the laboratory reactor, two gas flow rates, one in the Stokes region for a packed bed and one in the non-Stokes region, were investigated to give a significant difference in gas-solid mass transfer rates.

Initially, a 12.7-cm-long bed (20.6 g.) of dregs from Champion (C) was run at 100°C with 600 mL/min of feed gas containing 80 ppm H<sub>2</sub>S. The breakthrough time was 350 minutes. Because this was inconveniently long and would excessively use up the bottled feed gas, the bed size was reduced to 5.1 cm (8.4 g.). With this standard bed size, the run conditions became:

Temperature (°C):	100, 200
Flow Rate (mL/min.)	600, 1200
TRS Concentration (ppm)	5, 40, 80
O <sub>2</sub> Concentration (%)	4
Dregs Type	underflow, dregs filter

Typical breakthrough curves are shown in the figures below.

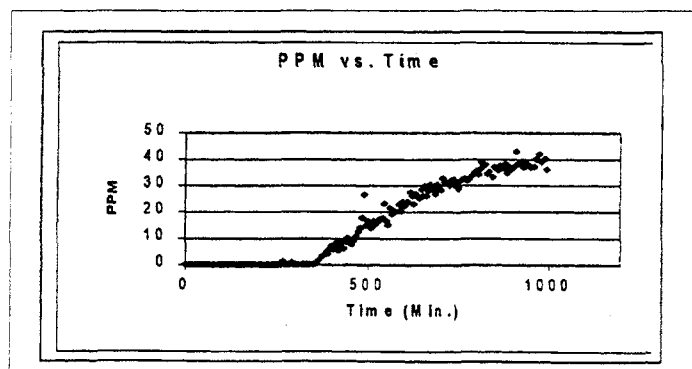


Figure 2. – Run 1 Conditions: 100°C, 600 mL/min, 80 ppm H<sub>2</sub>S, 12.7-cm bed (C)

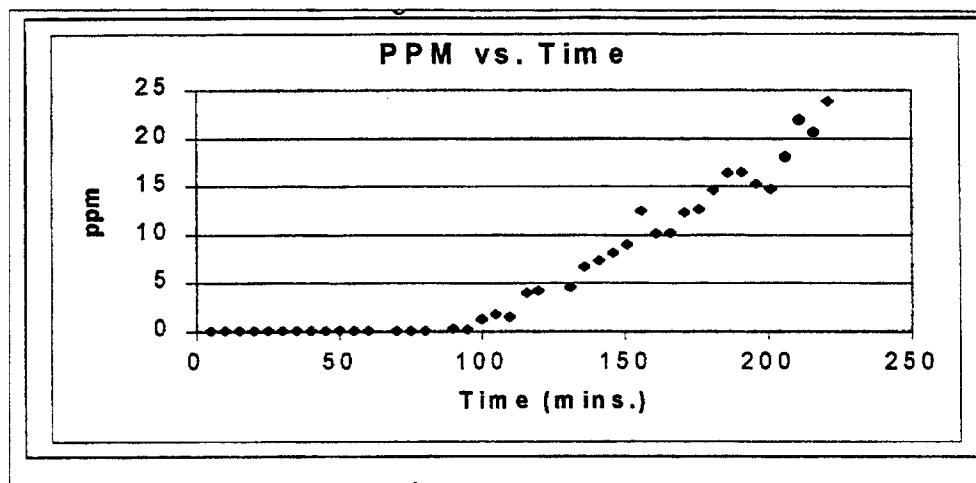


Figure 3. – Run 5 Conditions: 100°C, 600 mL/min, 80 ppm H<sub>2</sub>S, 5.1-cm bed (M)

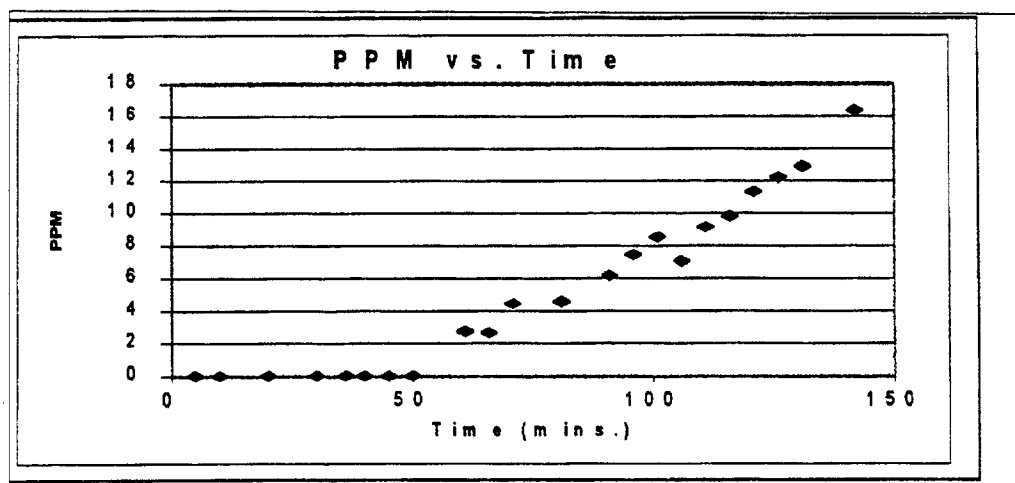


Figure 4. – Run 9 Conditions: 100°C, 1200 mL/min, 40 ppm H<sub>2</sub>S, 5.1-cm bed (C)



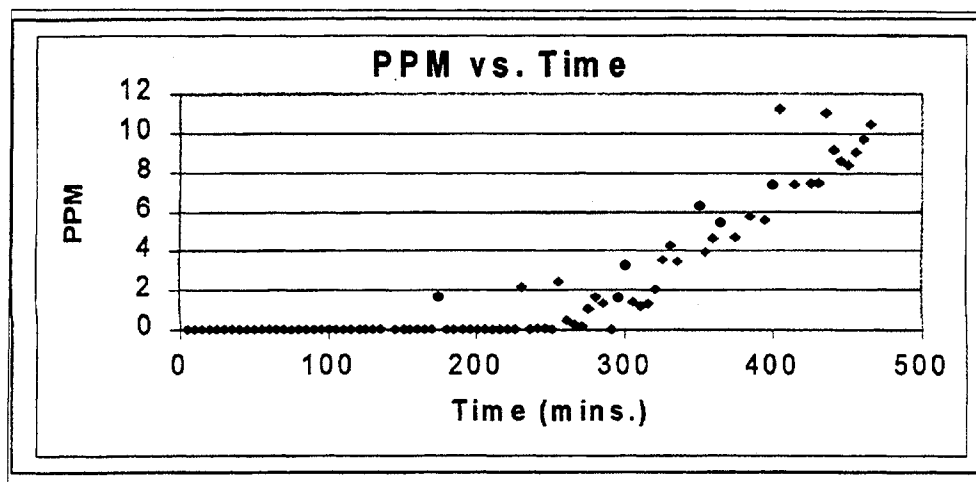


Figure 5. – Run 6 Conditions: 200°C, 600 mL/min, 80 ppm, 5.1-cm bed (M)

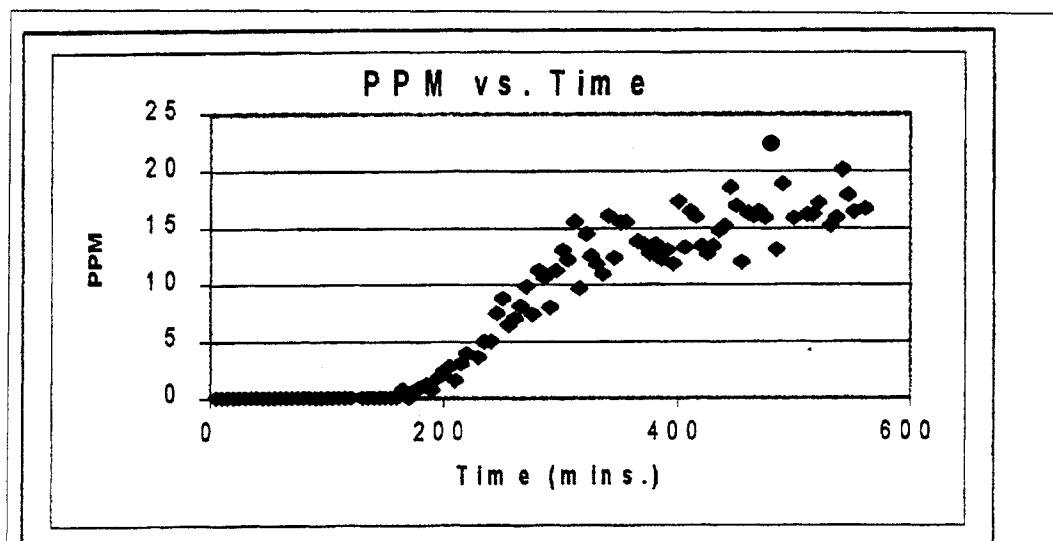


Figure 6. – Run 10 Conditions: 200°C, 1200 mL/min, 40 ppm H<sub>2</sub>S, 5.1-cm bed (C)

Results are summarized below in Table 1 for breakthrough time and bed capacity, which is defined as the weight of H<sub>2</sub>S removed up to the point of breakthrough per weight of dregs used.

Reproducibility in breakthrough times is seen in Runs 99, 100, 101, 105, and 106. The average was 152 minutes, with a standard deviation of 71 minutes. Runs 4 and 102, which were duplicates performed by different technicians, gave an average of 639 minutes with a standard deviation of 87. Experimental uncertainty comes not only from

variations in the normal operating variables but also in the sampling of dregs charged to the reactor; dregs homogeneity was not checked.

**Table 1 – Bed Performance Data for Breakthrough Time and Bed Capacity**

Run Des.	Bed Type (Mill)	Temp (°C)	Flow Rate (mL/min)	Feed Conc. (ppm)	Time (min)	H <sub>2</sub> S Removed (g.)	Capacity (g.H <sub>2</sub> S/g.Ds)
4	C	200	600	80	700	0.0510	0.00607
102	C	200	600	80	577	0.0420	0.00500
10	C	200	1200	40	380	0.0277	0.00330
7	C	200	600	40	830	0.0302	0.00360
3	C	200	600	5	2830	0.0129	0.00153
101	C	100	600	80	226	0.0165	0.00196
105	C	100	600	80	221	0.0161	0.00192
106	C	100	600	80	142	0.0103	0.00123
100	C	100	600	80	105	0.0077	0.00091
99	C	100	600	80	66	0.0048	0.00057
9	C	100	1200	40	50	0.0036	0.00043
8	C	100	600	40	160	0.0058	0.00069
2	C	100	600	5	1130	0.0051	0.00061
6	M	200	600	80	250	0.0182	0.00217
5	M	100	600	80	100	0.0073	0.00087
115	W	200	600	80	86	0.0063	0.00075
98	W	100	600	80	10	0.0007	0.00009

Key: C = Champion dregs  
W = Weyerhaeuser dregs  
M = MacMillan-Bloedel dregs

The effect of temperature on the breakthrough time and capacity of the Champion dregs for H<sub>2</sub>S removal was shown by comparing results at a given flow rate and TRS feed concentration for 100° and 200°. Raising the temperature from 100 to 200°C increased the capacity by a factor of 3 to 7 at both flow rates and all corresponding feed concentrations.

The effect of gas flow rate on the breakthrough time and (Champion) dregs capacity for H<sub>2</sub>S removal is shown in Table 1. At both temperatures, doubling the feed gas flow rate decreased the breakthrough times by a factor of about 3, but the capacities decreased only slightly. These are not considered significant because of a lack of duplication.

Run results also showed the effect of feed-gas concentration on the breakthrough time and dregs capacity for H<sub>2</sub>S removal. At both temperatures with the Champion dregs, raising the feed concentration from 5 to 40 ppm reduced the breakthrough time by 70-85%, while doubling the concentration from 40 to 80 ppm reduced it by less than

25%. The bed capacity at both temperatures showed an increase as the concentration increased from 5 to 80 ppm.

A multiple regression of the breakthrough data for the Champion dregs was run for the capacity as a function of temperature ( $T, ^\circ\text{C}$ ), flow rate (FR, mL/min), and feed concentration (C, ppm) to test for significant effects. The basic equation emerging from that data set is:

$$\text{Capacity} = 3.20 \times 10^{-5} T + 2.82 \times 10^{-5} C - 0.37 \times 10^{-6} \text{FR} - 0.003625$$

with an overall R-squared of 0.84. Applying the t-test to the three coefficients showed both concentration and temperature to be significant at the 95% confidence level.

**Table 2. – Bed Performance Data for Different Mill Dregs Samples**

Run Des.	Bed Type (Mill)	Temp ( $^\circ\text{C}$ )	Flow Rate (mL/min)	Feed Conc. (ppm)	Time (min)	H <sub>2</sub> S Removed (g.)	Capacity (g. H <sub>2</sub> S/g. Ds)
4	C	200	600	80	700	0.0510	0.00607
102	C	200	600	80	577	0.0420	0.00500
6	M	200	600	80	250	0.0182	0.00217
115	W	200	600	80	86	0.0063	0.00075
101	C	100	600	80	226	0.0165	0.00196
105	C	100	600	80	221	0.0161	0.00192
106	C	100	600	80	142	0.0103	0.00123
100	C	100	600	80	105	0.0077	0.00091
99	C	100	600	80	66	0.0048	0.00057
5	M	100	600	80	100	0.0073	0.00087
98	W	100	600	80	10	0.0007	0.00009

The variation with dregs type (see Table 2) was quite striking. At 200° the Champion dregs off the precoat filter were 2.5 times more reactive than the MacMillan-Bloedel underflow dregs (containing no lime mud precoat solids); at 100° the factor was 1.5. The Weyerhaeuser dregs (also off the precoat filter) were much less effective than either the Champion or the MacMillan-Bloedel dregs.

Because the Weyerhaeuser dregs appeared to contain a greater fraction of lime mud precoat material than did the Champion dregs, a chemical analysis of each of the fresh dregs samples was obtained so that results could be compared and hopefully rationalized. The data from Table 3 indicate that the Champion dregs contain the largest amount of organic carbon, which would support a claim that adsorption is one mechanism for the H<sub>2</sub>S removal observed in this work. The Champion dregs also contain the largest amount of sodium, which could be involved in neutralization reactions, supporting that mechanism. The high calcium and carbonate (inorganic carbon) content of the Weyerhaeuser dregs, together with its low sodium and organic carbon content, strongly suggest that the majority of this sample was lime mud precoat solids. Since it

would appear that the Weyerhaeuser sample was deficient in dregs content, this would justify the fact that these dregs performed poorly relative to the other two mill sources.

**Table 3. – Elemental Analyses of Dregs**

Element	Weight Percent (Dry Basis)		
	Champion	MacMillan-Bloedel	Weyerhaeuser
Ca	19.95	23.15	34.70
Mg	2.13	2.78	0.77
Mn	1.03	1.23	0.08
Fe	0.32	0.92	0.07
Na	9.41	6.68	0.82
Al	0.31	0.49	0.07
Si	0.23	0.06	0.06
S	1.93	1.72	0.13
K	0.83	0.41	0.03
Org.C	7.37	5.05	2.05
Inorg.C	8.67	8.57	11.13

Initially, regeneration of spent dregs was attempted using air at 200°C as a possible oxidizing agent. This was tried with two feed concentrations at a flow rate of 600 mL/min; both were unsuccessful, as shown in Table 4. In both cases, breakthrough times of the “regenerated” beds were less than 5% of the expected fresh-bed value.

**Table 4. – Regenerated Bed Performance Data**

Run Des.	Bed Type	Temp (°C)	Flow Rate (mL/min)	Feed Conc. (ppm)	Time (min)	H <sub>2</sub> S Removed (g.)	Capacity (g.H <sub>2</sub> S/g.Ds)
4	C	200	600	80	700	0.0510	0.00607
4R(O <sub>2</sub> )	C	200	600	80	20	0.0015	0.00017
7	C	200	600	40	830	0.0302	0.00360
7R(O <sub>2</sub> )	C	200	600	40	20	0.0007	0.00009
1	C	100	600	80	350*	0.0255*	0.00124
12R(OH)	C	100	600	80	136	0.0099	0.00118
115	W	200	600	80	86	0.0063	0.00075
117R(OH)	W	200	600	80	80	0.0058	0.00069
118R(OH)	W	200	600	80	5	0.0004	0.00004

Run Designation Key: R(O<sub>2</sub>) = regenerated with oxygen  
R(OH) = regenerated with caustic  
\* = large bed

A second method was tried that was much more successful. Regeneration of activated carbon has been accomplished using a 10% w/v NaOH solution at 90-95°C for 4 hours (5). The literature also reports that, based upon chemical thermodynamic equilibria, a weak caustic solution could regenerate scrubbing media that was calcium-based (11). Since the primary metal content of dregs is calcium, regeneration with a 10% w/v NaOH solution was attempted. The basic reactions involve  $H_2S$  with oxidized calcium salts to form CaS, followed by reaction with NaOH to form  $Na_2S$ . This method would be very compatible with the kraft liquor cycle, as the regenerating medium could be weak wash. The weak wash so used, now slightly higher in sulfide content, would continue to be recycled to the dissolving tank and not require any separate “clean-up” step. This would further close the sulfur loop in the liquor cycle, reducing the need for make-up sulfur while not generating a waste stream requiring treatment prior to disposal.

Spent dregs from Runs 1, 115, and 117 were reslurried in 10% w/v NaOH in water and gently heated to 95°C with stirring for four hours, then washed, dried, crushed, and sieved before reusing for TRS removal. At 100°C, the regenerated dregs (Run 12R) gave a nearly identical bed capacity to the fresh dregs (Run 1, which had a larger bed) and a breakthrough time nearly equal to the average of the times for fresh Champion dregs at the same run conditions and same bed size (see Table 2). At 200°C, the regenerated dregs from Run 115 also nearly duplicated the breakthrough time (Run 117R) for fresh dregs; however, a subsequent regeneration of Run 117R gave a very short breakthrough time (Run 118R) for the third sulfide reduction cycle, signifying inactive dregs for  $H_2S$  removal. Whether or not this result is valid is still an open question because there was no opportunity to duplicate it.

The odor-producing gases that make up kraft mill TRS emissions include, in order of decreasing amount, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Since the focus of this study was on the polar/acid gas  $H_2S$ , it was suggested that the nonpolar/nonacidic gas, dimethyl sulfide (DMS), also be investigated. Five runs with DMS were made using both Champion and MacMillan-Bloedel dregs under standard conditions shown to be effective with  $H_2S$ , namely 80 ppm feed concentration, 600 mL/min, 8.4 g. bed, and 100° and 200°C. In all cases, the DMS eluted with the product gas almost instantly at the feed concentration value; hence, there appeared to be no interaction of the DMS with the dregs particles, unlike the results with  $H_2S$ . We anticipate more favorable results when treating mill gases that contain significant water vapor. Alley (16) claims that if the relative humidity of the gas mixture stays above 70%, methyl mercaptan will be oxidized to DMDS, which in turn is adsorbed on carbonaceous material.

Commercialization of this approach to odor control presents concerns with pressure-drop requirements for the reactor, since the mill waste gases to be treated presently leave their stacks and vents at essentially atmospheric pressure. In the lab reactor, pressure drops were recorded using nitrogen at several flow rates through dregs beds ranging from 6.3 cm to 31.8 cm long. Results are summarized in Table 5, where values ranging from 0.55 to 0.95 kPa/cm were obtained. Consequently, in a mill situation, either a fan or a compressor would be required to move the gas through the

reactor. Depending upon the bed length required for a commercial installation, an alternative lower pressure-drop configuration, such as a fluidized bed or possibly use of pelletized dregs particles, may have to be considered.

**Table 5. – Pressure Drop per Unit Length of Dregs Bed**

Gas Flow Rate (mL/min)	Pressure Drop (kPa/cm)	Pressure Drop (psi/ft)
250	0.55	2.4
500	0.55	2.4
750	0.8	3.6
1000	0.95	4.2
1250	0.95	4.2

In an attempt to gain greater insight into the mechanism of sulfide removal, samples of both fresh unreacted dregs and spent dregs after the bed experienced breakthrough were analyzed for sulfur content using an acid digestion procedure and Inductively Coupled Plasma. Unexpectedly, slightly less sulfur was detected in the spent dregs. Subsequent calculations showed that the expected sulfur pickup would be so small that sampling and analysis errors could easily mask the expected increase.

A possible change in dregs pH was checked by measuring it before and after reaction. Values of 11.6 were recorded for both samples. The form of the sulfur present in the product gas from the reactor after breakthrough was checked for selected H<sub>2</sub>S and DMS runs. In both cases, the form of the sulfur did not change upon passing through the bed; hence, there was negligible or no oxidation.

## ENGINEERING CONSIDERATIONS

What do the rate data generated thus far mean when applied to a mill operation? If we consider the recovery boiler stack alone, knowing that it emits about half of all TRS emissions from today's typical kraft mill [13], we can calculate what a "worst case" fixed-bed installation for odor elimination from this source might look like.

For a 1000 T/D pulp mill with a low odor-recovery boiler being fed 75% solids black liquor and 10% excess air, typical daily "production" rates of TRS and dregs are calculated to be 34 kg and 5,900 kg, respectively [10]. Using a limiting superficial gas velocity through the packed-bed reactor of 0.24 m/sec at 200°C, a total bed cross-sectional area of 42 m<sup>2</sup> is required to handle the 6,230 m<sup>3</sup>/min of flue gas. This reactor could be a "bundle" of twenty-three 1.5-m-diameter tubes; for an assumed space time (bed volume/volumetric gas feed rate) of one second, the length of the tubes would be 2.44 m, giving a total bed volume of 104 m<sup>3</sup>. Assuming the specific gravity of dregs to be 0.7, this volume would contain 72,640 kg of dregs (12 days' production).

Assuming the capacity of dregs at these conditions to be 0.003 g.TRS/g.dregs, two of the 23 reactor units would have to be regenerated each day. On a rotating replacement cycle of two units per day, only one regeneration would be required of each reactor unit before its spent dregs would be sent to the landfill. Regeneration in a mill setting would involve leaving the dregs bed in place and flushing with weak wash for a period of time (to be determined). The daily production of fresh dregs would then replace two units that have gone through two cycles of TRS removal (and one regeneration cycle).

The overriding factor in this scenario is the huge volumetric flow rate of flue gas, which demands such a sizeable reactor cross-sectional area. It appears that the daily TRS and dregs production rates are compatible with the capacities and removal rates reported in this work. At a pressure drop of over 0.9 kPa/cm, a reactor  $\Delta P$  of over 220 kPa is a genuine concern and may suggest looking at an alternative reactor design such as a fluidized bed, or possibly making larger-sized dregs particles through pelletization.

Finally, these calculations have been based totally on  $H_2S$ . Removal of DMS was not successful, and DMDS and methyl mercaptan were not investigated. Together, these three on a mole basis occur in about the same amount as  $H_2S$  [14]. The gas streams emitting from the mill also contain water vapor,  $CO_2$ , and other gases. Since reduced sulfur compounds interact differently with a carbonaceous adsorbent with or without the presence of water vapor, actual performance of dregs as a TRS scavenger should be demonstrated at a mill with samples of actual gas mixtures to uncover any possible chemical interaction effects. This work is presently under way.

## CONCLUSIONS

1.  $H_2S$  can be removed from a flowing gas mixture down to nondetect concentration levels by a fixed bed of mill dregs particles. Data reproducibility was good, considering the complex composition of dregs. Dimethyl sulfide was not effectively removed by the same bed of dregs.
2. Bed capacity and breakthrough time increased with temperature; on the other hand, an increase in  $H_2S$  feed concentration was accompanied by an increase in capacity and a decrease in breakthrough time. Increasing the rate of gas feed lowered the breakthrough time but had little impact on capacity.
3. Bed capacity was sensitive to the source of the dregs used. The Champion dregs were more reactive than the MacMillan-Bloedel dregs, which were more reactive than the Weyerhaeuser dregs. Compositional differences in organic carbon and calcium could explain these differences.
4. Bed regeneration was effective at least one time using a dilute caustic solution. In a mill situation, weak wash could be the regenerating medium and thus would more tightly close up the mill's sulfur balance without generating a liquid effluent stream needing its own treatment.

5. Preliminary engineering calculations for treating a typical recovery boiler stack indicated technical feasibility, but pressure-drop considerations pointed out the need for larger dregs particles or an alternative reactor type with lower pressure-drop characteristics, such as a fluidized bed.
6. More work is needed with actual mill gases to confirm TRS reduction degrees and rates in the presence of the other stream components, including water vapor and CO<sub>2</sub>. More laboratory work is needed to identify the actual mechanism by which dregs can remove TRS gases from a gas mixture.

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